

Permanent Bubble Arrays from a Cross-Linked Poly(*para*-phenyleneethynylene): Picoliter Holes without Microfabrication

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We describe arrays of self-assembled picoliter holes^{1–7} fabricated from poly(*para*-phenyleneethynylene) (PPE, **4**). The holes are formed by heating self-assembled bubble arrays (from **4**) to 300 °C. They will be useful as picoliter beakers.

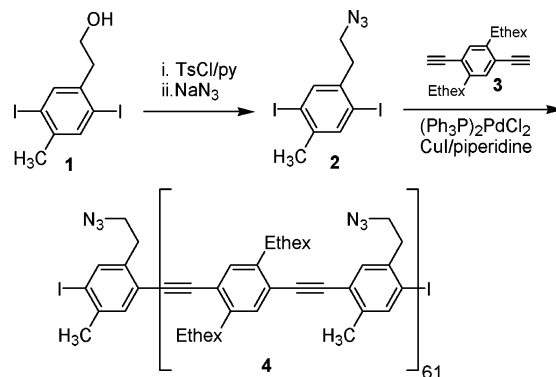
Picoliter beakers^{1–8} are of importance in analytical and bioanalytical chemistry. They allow isolating very small volumes of liquid or single cells and interrogating them by either electrochemical or enzymatic methods. The manipulation of such small volumes is performed with micropipets and microelectrodes and uses enzymatic assays and cyclic voltammetry/ampereometry. However, the fabrication of picoliter beakers or picoliter vials is not trivial and often involves tedious photolithographic methods that are expensive and not commonly available to chemists. It was therefore of fundamental and practical interest to develop a simple nonphotolithographic access to picoliter vials.

Breath figures form if moist air comes in contact with a cold surface. Lord Rayleigh⁹ showed that breath figures are microscopic water droplets that condense onto a cold substrate. Such breath figures are fleeting in their existence, forming on cold solids and liquid surfaces. A use for breath figures stems from the discovery that solutions of polymers in fast evaporating solvents generate hexagonally ordered bubble arrays when moist air is used to evaporate the solvent. On complete evaporation, the remaining polymer matrix exhibits an ordered bubble array, a fossilized version of the breath figure.¹⁰ Very different polymers, such as polystyrene¹¹ and rod coil block copolymers,¹² as well as PPEs and polythiophenes,¹³ form self-assembled bubble arrays from breath figures.

Such bubble arrays are usually interconnected, and the polymer scaffold can be dissolved in organic solvents. For an application such as picoliter vials, one would like to have bubble arrays that are cross-linked, rendering them insoluble. Recently, Shimomura¹⁴ et al. have utilized an imidization reaction to make a bubble array insoluble and more permanent. Herein we present a simple way of fabricating stable, fluorescent, noninterconnected, and insoluble picoliter beakers by heating bubble arrays of **4** to 300 °C.

Starting from the alcohol **1** (Scheme 1), toluenesulfonyl chloride in pyridine converts the hydroxyl group into a tosylate. Reaction with sodium azide furnishes the monomer **2** in 64% yield. Copolymerization of **2** with **3** (0.2 mol % (Ph₃P)₂PdCl₂, 0.2 mol % CuI) in a mixture of piperidine and THF furnishes the polymer **4** in a 95% yield and with a degree of polymerization (*P_n*) of 61 and a polydispersity (*M_w/M_n*) of 2.3, relative to a polystyrene standard.¹⁵ The polymer **4** shows normal absorption and emission spectra, identical to those of reported dialkyl-PPEs.¹⁵ Under the reaction conditions, the azide group is unreactive and does not interfere with the alkyne units.¹⁶

Scheme 1. Synthesis of an Azide-Substituted PPE **4**



DSC of **4** shows exothermic transitions at 180 °C (24.7 kcal/mol/repeating unit) and 213 °C (1.7 kcal/mol/repeating unit). Neither glass transition nor melting is observed for this polymer.

Smooth thin films of **4** are obtained upon spin casting, and bubble arrays are obtained when **4** is subjected to standard breath figure forming methods.^{9,10,13} This method consists of taking a very dilute polymer solution in a volatile solvent and passing moist air across the solution surface. This evaporation of the solvent is accompanied by cooling and the formation of water droplets that lead the bubble arrays after all of the solvent has disappeared. Solutions of approximately 0.1–0.5 weight % of **4** in carbon disulfide give well-developed arrays. A typical example is shown in Figures 1 and 2 (top each).^{9,10,13} Since **4** features multiple azide groups in its side chains, it is expected to cross-link at high temperatures; we were curious to find out if the bubble structure was preserved. On heating the arrays to 300 °C for 1 h we find that the fluorescence of the cross-linked material has diminished to approximately 10% of its original value, and it is now insoluble in carbon disulfide. This thermoset can be peeled off the glass slide to give a free-standing film. According to IR, the azide peak has almost disappeared. We presume that multiple [3 + 2] cycloadditions have taken place.¹⁶ There are significant differences in the microstructure between the unheated and the heated films. It is evident from Figure 1 that the air bubbles in the (unheated) arrays are interconnected while those in the heated one are not. Upon heating, the polymer scaffold softens and collapses on itself to generate a thinner film with isolated holes, while at the same time cross-linking preserves the microstructure. This easily generated structure, quite remarkably, strongly resembles lithographically microfabricated “picoliter beaker” arrays!

These thermolyzed bubble arrays have the potential to work as templates for directed self-assembly of colloidal particles¹⁷ and for the formation of polysiloxane microlenses¹⁸ by filling the collapsed bubbles with a liquid oligosiloxane polymer followed by

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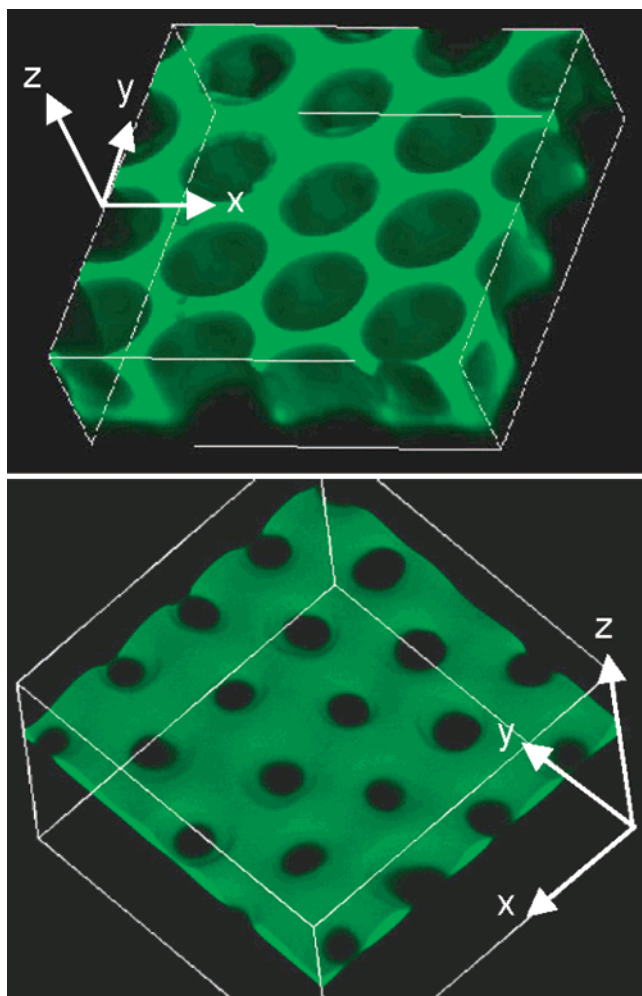


Figure 1. Laser scanning confocal micrographs of the bubble arrays. Top: Bubble arrays formed from polymer **4** in carbon disulfide. Image dimensions are $15.2 \mu\text{m} \times 15.2 \mu\text{m} \times 4.7 \mu\text{m}$. Bottom: Same bubble arrays after heating of the sample for 60 min to $300 \text{ }^\circ\text{C}$. Image dimensions are $21.3 \mu\text{m} \times 21.3 \mu\text{m} \times 21.3 \mu\text{m}$. Visible is the flattening of the sample, due to shrinking by softening and cross-linking.

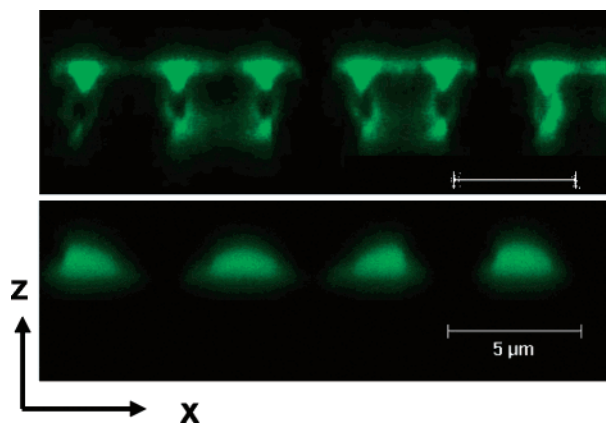


Figure 2. Cross section of the bubble array. *x* and *z* axes are identical to those in Figure 1. Top: Interconnected bubble arrays from **4** "as obtained". Bottom: The array was heated from 25 to $300 \text{ }^\circ\text{C}$ for 60 min, and the confocal laser micrograph was taken after cooling the sample to ambient temperature. Scale bar = $5 \mu\text{m}$. The shrinking of the bubble arrays in the third dimension (thickness direction) is visible. Cup-shaped, isolated picovials or picoliter beakers have formed.

Pt-catalyzed cross-linking.¹⁹ The use of the cross-linked azide-PPE microcups as matrix is particularly interesting, because arrays of

microlenses could be obtained by filling, curing, and peeling. Such arrays could functionally be similar to the calcite microlenses that are found on the arms of brittle stars.²⁰

In conclusion, we have prepared self-assembled bubble arrays from an azide-substituted PPE **4**. Thermal cross-linking of these arrays leads to their collapse under formation of self-assembled picoliter hole arrays with a density of approximately 40 000 holes/ mm^2 . These microstructures have great potential as microanalytical tools and as matrices for the fabrication of microlens or micro-OLED arrays.

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Supporting Information Available: Synthesis and characterization of polymer **4** and monomer **2** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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